

ORIGIN OF MOLECULAR OXYGEN IN COMET 67P/CHURYUMOV-GERASIMENKO

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ABSTRACT

Molecular oxygen has been detected in the coma of comet 67P/Churyumov-Gerasimenko with abundances in the 1–10% range by the ROSINA-DFMS instrument on board the Rosetta spacecraft. Here we find that the radiolysis of icy grains in low-density environments such as the presolar cloud may induce the production of large amounts of molecular oxygen. We also show that molecular oxygen can be efficiently trapped in clathrates formed in the protosolar nebula, and that its incorporation as crystalline ice is highly implausible because this would imply much larger abundances of Ar and N₂ than those observed in the coma. Assuming that radiolysis has been the only O₂ production mechanism at work, we conclude that the formation of comet 67P/Churyumov-Gerasimenko is possible in a dense and early protosolar nebula in the framework of two extreme scenarios: (1) agglomeration from pristine amorphous icy grains/particles formed in ISM and (2) agglomeration from clathrates that formed during the disk’s cooling. The former scenario is found consistent with the strong correlation between O₂ and H₂O observed in 67P/C-G’s coma while the latter scenario requires that clathrates formed from ISM icy grains that crystallized when entering the protosolar nebula.

Subject headings: comets: general – comets: individual (67P/Churyumov-Gerasimenko) – solid state: volatile – methods: numerical – astrobiology

1. INTRODUCTION

The Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) Double Focusing Mass Spectrometer (DFMS) on board the Rosetta spacecraft (Balsiger et al. 2007) enabled the detection of O₂ in the coma of comet 67P/Churyumov-Gerasimenko (67P/C-G) with local abundances in the 1–10% range and a mean value of $3.80 \pm 0.85\%$ (Bieler et al. 2015). A subsequent reinvestigation of the 1P/Halley data from the Giotto Neutral Mass Spectrometer (NMS) also indicates that the coma of comet 1P/Halley should contain O₂ with an abundance of $3.7 \pm 1.7\%$ with respect to water, suggesting that this molecule may be a rather common parent species in comets (Rubin et al. 2015a).

To investigate the origin of O₂ in 67P/C-G, Bieler et al. (2015) considered the possibility of O₂ production via the radiolysis of water ice incorporated within the nucleus. Based on 67P/C-G’s known orbital history, they estimated that any O₂ produced during the residence time of 67P/C-G in the Kuiper Belt was quickly lost during the first pass or two around the Sun. The authors further found that radiolysis on closer orbit to the Sun would most likely only affect the top few micrometres

of the nucleus’ active surface. In this case the O₂/H₂O ratio produced in these conditions would decrease with depth. Because they did not observe any variation of the O₂/H₂O ratio during the sampling period, Bieler et al. (2015) ruled out the hypothesis of O₂ production via the radiolysis and determined that O₂ must have been incorporated into 67P/C-G at the time of its formation in the protosolar nebula (PSN).

In order to explain how O₂ could have been incorporated into the ices of 67P/C-G, we investigate here the radiolysis hypothesis at epochs prior to the formation of comets, when icy grains were the dominant solid phase of the outer PSN. Furthermore, we examine the different trapping scenarios of O₂ that could explain its presence. Because some recent works suggest that this comet may have been accreted from a mixture of clathrates and pure crystalline ices formed in the PSN (Mousis et al. 2016; Luspai-Kuti et al. 2016), we study the propensity for O₂ trapping in clathrates, and also evaluate if its condensation as pure crystalline ice is consistent with the comet’s inferred composition. Among all these investigated mechanisms, we find that clathration of O₂ is efficient in the PSN and that radiolysis can explain the formation of O₂ and its stabilization in icy grains. However, to produce enough O₂ molecules, the radiolysis of icy grains must have happened in a low density environment such as the presolar cloud.

2. O₂ FORMATION VIA RADIOLYSIS

We first investigate the possibility of radiolytic production of O₂ in icy grains present in the outer PSN prior to their agglomeration by 67P/C-G. The energy available for radiolysis is provided by the galactic Cosmic Ray Flux (CRF) impacting icy grains. In the following, since galactic CR can penetrate into water ice down to depths of a few tens of meters (Cooper et al. 1998), we only

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consider icy grains with sizes below this limit, implying that no H_2O ice can be out of reach of radiolysis. In our calculations, we use the energy range and CRF distribution from Yeghikyan (2011) and Cooper et al. (2003), respectively. The CRF energy dose absorbed by icy grains located at 30 AU from the sun is within the $\sim(5\text{--}60)\times 10^{16}$ eV kg^{-1} yr^{-1} range, depending on the disk's surface density (between 10 and 10^3 g cm^{-2} ; see Hersant et al. 2001).

O_2 is produced by radiolysis of water ice through the chemical reaction $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$, with an amount of energy needed to alter one H_2O molecule $W_r = 235$ eV (Johnson 1991). H_2 is then rapidly lost from the water ice due to its fast diffusion. Further reactions with O_2 are precluded because the diffusion of these molecules is slowed down by the disk's low temperatures (Johnson 1990). We have thus assumed that all the energy absorbed by water ice is used to form O_2 . To reach the molecular ratio $\text{O}_2/\text{H}_2\text{O}$ (1–10%) measured by Bieler et al. (2015) in 67P/C-G, cosmic rays must alter twice as many H_2O molecules in icy grains. The time τ needed to reach this ratio is then given by:

$$\tau = \frac{W_r \cdot N_A}{E_{CR} \cdot M_{\text{H}_2\text{O}}} \times f_{\text{H}_2\text{O}} \quad (1)$$

where N_A (mol^{-1}) is the Avogadro constant, $M_{\text{H}_2\text{O}}$ (kg mol^{-1}) is the molar mass of water, E_{CR} ($\text{eV kg}^{-1} \text{yr}^{-1}$) is the CRF energy dose received by water ice and $f_{\text{H}_2\text{O}}$ is the fraction of altered H_2O molecules, which corresponds to two times the fraction of O_2 produced.

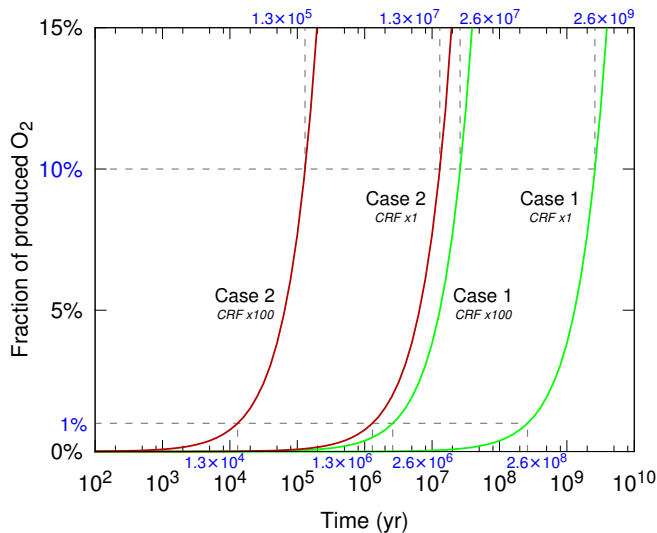


FIG. 1.— Time evolution of the fraction of O_2 molecules produced by cosmic rays in an icy grain. Case 1 (green curves) considers the irradiation of an icy grain placed at 30 AU in the PSN. Case 2 (red curves) considers the irradiation of an icy grain located in a low density environment ($\sim 10^{-3}$ g cm^{-2}). Two CRF values are explored in each case, namely 1 and 100 times the nominal CRF value (see text).

Figure 1 shows the results of our calculations. An O_2 fraction in the 1–10% range is reached in $\sim 0.25\text{--}2.5$ Gyr at the aforementioned nominal CRF value (Case 1). These extremely long time periods are incompatible with

the lifetime of icy grains in the PSN (a few 10^4 yr; Weidenschilling and Cuzzi 1993). If icy grains have grown to sizes larger than tens of meters in the PSN, then the deepest layers should remain unaltered. In this case, even longer timescales would be needed for O_2 formation. However, the CRF may have undergone significant enhancements throughout the history of the solar system, by a factor ~ 3 during its passages through the Milky Way's spiral arms (a few tens of Myr every 400–500 Myr; Effenberger et al. 2012; Werner et al. 2015; Alexeev 2016), or even by a factor of ~ 100 during a few kyr because of a close supernova explosion (< 30 pc; Fields & Ellis 1999). Such enhancements can decrease the time needed to form O_2 by up to a factor 100, which is still too long for our consideration.

We also consider the possibility of an icy grain receiving the maximum CRF energy dose estimated by Yeghikyan (2011), namely $\sim 1.20 \times 10^{20}$ eV kg^{-1} yr^{-1} . This value leads to a time τ in the $\sim 1\text{--}10$ Myr range (see case 2 of Fig. 1), or $\sim 10\text{--}100$ kyr with a CRF enhanced by a factor 100. However, such a high value of E_{CR} corresponds to a surface density of 10^{-3} g cm^{-2} , which can only be reached in molecular clouds. In such environments, the column densities would be low enough to form 1–10% of O_2 in the icy grains even on very short timescales. Therefore, to incorporate significant amounts of O_2 produced via radiolysis of icy grains, cometary grains must have formed in the presolar cloud prior to disk formation.

3. O_2 STABILITY IN WATER ICE

An important question is whether O_2 molecules produced via radiolysis of ice grains can remain stabilized within the water icy matrix of 67P/C-G. The stabilization energy is defined as the difference between the energy of the system of O_2 interacting with the ice and the sum of the energies of the pure ice and O_2 at infinite separation. To investigate this problem, a sampling of the representative structures of O_2 in solid water ice has been obtained using a strategy based on first principle periodic density functional theory quantum calculations, that has been proven to be appropriate for modeling bulk and surface ice structures (Lattalais et al. 2011; 2015; Ellinger et al. 2015). Among the different forms, we considered the apolar variety of hexagonal ice I_h because these structures have a balanced distribution of alternating hydrogen and oxygen avoiding computational artifacts for surface optimizations and at the same time reproduce the bulk properties (Casassa et al. 2005). How O_2 behaves as a function of the number of H_2O molecules removed is illustrative of the storage capability of the ice as a function of porosity. The results of our calculations, performed using the Vienna ab initio simulation package (VASP) (Kresse & Hafner 1993; 1994), are presented below:

1. Starting with no H_2O removed, i.e., the pure crystalline ice, we found no stabilisation for the inclusion of O_2 in the hexagonal lattice. It is in fact an endothermic process.
2. With one H_2O removed, and replaced by one O_2 , we have a substitution structure whose stabilisation, in the order of 10^{-3} eV, is meaningless.

3. With 2, 3, and 4 adjacent H_2O molecules removed from the hexagonal lattice we obtained well defined cavities that, after reconstruction, show different shapes according to the positions of the entities removed. The stabilization energies were found to be on the order of 0.2–0.3 eV, going to 0.4–0.5 eV for an embedded O_2 dimer. A typical structure of embedding is illustrated in Fig. 2 where O_2 is stabilized with an energy of ~ 0.23 eV. This energy is of the order of that of a water dimer which means that the presence of O_2 should not perturb the ice structure until it is ejected into the coma via sublimation with the surrounding H_2O molecules.

It should be stressed that the formation of one O_2 requires at least the destruction of two H_2O . The present simulation is fully consistent with the aforementioned radiolysis hypothesis, where the irradiation process is at the origin of both the formation of O_2 and the development of the cavity in which it remains sequestered. Similar results are obtained in the case of O_2 stabilization in amorphous ice.

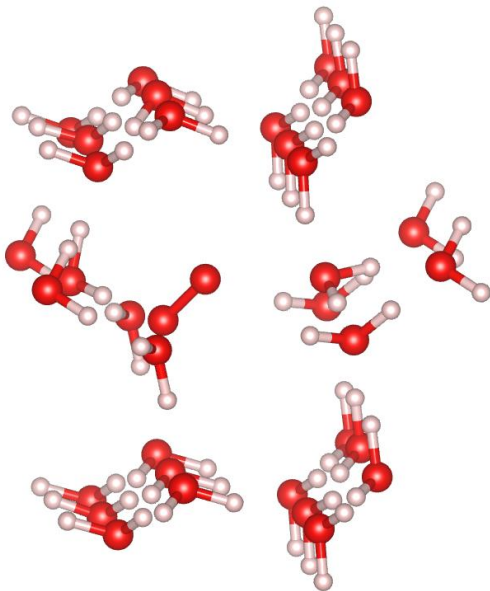


FIG. 2.— Side view of O_2 embedded in a cavity inside compact amorphous ice. The cavity corresponds to a void of 3 H_2O molecules from an hexagonal apolar lattice.

4. O_2 CLATHRATION IN THE PSN

One possible source of O_2 in the nucleus of 67P/C-G is the trapping of O_2 in clathrates that formed in the PSN prior to having been agglomerated by the comet as it formed. This is supported by recent works showing that the Ar/CO and N_2 /CO ratios and the time variation of other volatile species measured in 67P/C-G’s coma are found to be consistent with the presence of clathrates in its nucleus (Mousis et al. 2016; Luspay-Kuti et al. 2016). To investigate the amount of O_2 that could have been trapped in clathrates and now be present in 67P/C-G, we use the same statistical thermodynamic model as the one described in Mousis et al. (2010, 2016), which is used to

estimate the composition of these crystalline structures formed in the PSN. To evaluate the trapping efficiency of O_2 , we consider a gas constituted of O_2 and CO. After H_2O , CO is one of the dominant gases found in 67P/C-G (Le Roy et al. 2015) and in most of comets (Bockelée-Morvan et al. 2004). The Kihara parameters for the molecule-water interactions employed in our calculations are derived from Mohammadi et al. (2003) for O_2 and from Mohammadi et al. (2005) for CO. These represent the most recent sets of data found in the literature for the two species. We refer the reader to the model description provided in Mousis et al. (2010) for further details.

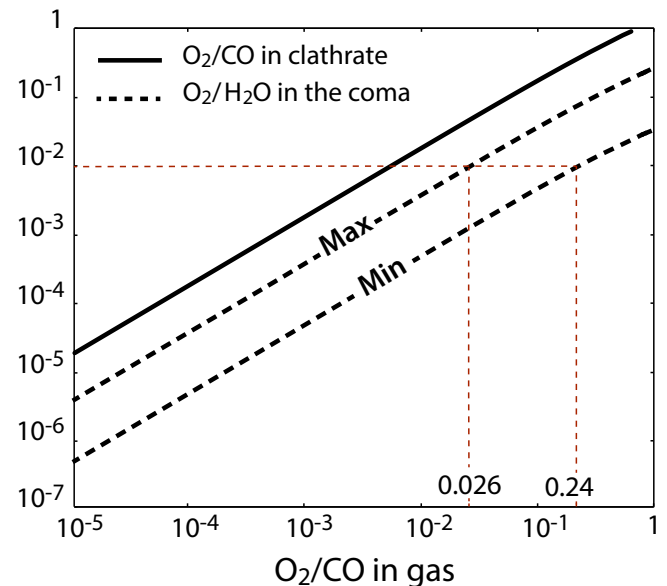


FIG. 3.— O_2 /CO ratio in clathrates formed at 45 K and the corresponding O_2 /H $_2$ O ratio in the coma, as a function of the co-existing O_2 /CO ratio in the PSN gas phase. The “Min” and “Max” labels correspond to calculations of the O_2 /H $_2$ O ratio in 67P/C-G’s coma, assuming that the CO/H $_2$ O abundance is between 2.7 and 21% (see text). The vertical red dashed lines represent the O_2 /CO ratio in the PSN gas phase needed to form clathrates giving 1% O_2 relative to H_2O in the coma.

When clathrates destabilize in the nucleus, the trapped volatiles are released prior to water sublimation, implying that the water vapor measured at the time of the O_2 sampling by ROSINA should be derived from the vaporization of crystalline ice layers located closer to the surface. Hence, the O_2 depletion is better quantified by comparing the O_2 /CO ratio in clathrates and the coma value since these two species are expected to be released simultaneously from destabilized clathrates. Figure 3 represents the value of the O_2 /CO ratio in structure I clathrates⁷ as a function of the O_2 /CO ratio in the co-existing gas phase at a chosen disk’s temperature of ~ 45 K. This value is within the temperature range needed for clathrates to form in the PSN from a gaseous mixture of protosolar composition that reproduces the Ar/CO and N_2 /CO ratios measured in 67P/C-G’s coma (Mousis et al. 2016). We find that, whatever the O_2 /CO ratio considered for the initial PSN gas phase, it is enriched by a

⁷ Both O_2 and CO molecules are expected to form this structure (Mohammadi et al. 2003, 2005).

factor of ~ 1.4 – 1.8 in the formed clathrate. Figure 3 also shows that the O_2/CO ratio must be in the 0.026 – 0.24 range in the PSN gas phase for the clathrate trapping mechanism to agree with the measured range of $\text{O}_2/\text{H}_2\text{O}$ in the coma ($\sim 1\%$), assuming that all cavities are filled by guest molecules and that the $\text{CO}/\text{H}_2\text{O}$ abundance ratio in the coma corresponds to the sampled value (~ 2.7 – 21% ; Le Roy et al. 2015). This range of O_2/CO ratios is consistent with values obtained at distances beyond ~ 5 AU in a T Tauri disk (Walsh et al. 2015). Therefore, our calculations show that the clathration of O_2 in the PSN is a realistic mechanism to account for the $\text{O}_2/\text{H}_2\text{O}$ ratio observed by ROSINA in 67P/C-G’s coma.

5. O_2 CONDENSATION IN THE PSN

An alternative possibility for the observed presence of O_2 in the coma of 67P/C-G is that the O_2 could have been agglomerated as pure crystalline ice by the nucleus forming at cooler PSN temperatures than those required for clathration. To investigate this scenario, we calculated the temperature dependence of the equilibrium curves of O_2 , CO, N_2 and Ar pure crystalline ices via the use of the polynomial relations reported by Fray & Schmidt (2009). To derive the partial pressures for each gas, we assumed that O, C, N and Ar exist in protosolar abundances in the PSN (Lodders et al. 2009), with all C and all N in the forms of CO and N_2 , respectively. The partial pressure of O_2 is derived from the O_2/CO gas phase ratio ($\sim 33\%$) predicted beyond the snowline of a T Tauri disk via an extensive chemical model (Walsh et al. 2015). The equilibrium curves of O_2 , CO, N_2 and Ar pure crystalline ices are represented along with the equilibrium curve of the CO– N_2 –Ar multiple guest clathrate proposed by Mousis et al. (2016) to explain 67P/C-G’s composition, as a function of the total PSN pressure in Fig. 4. Because the CO– N_2 –Ar multiple guest clathrate is by far dominated by CO (see Fig. 1 of Mousis et al. 2016), we assume that its partial pressure is the same as for CO crystalline ice. The equilibrium curve of the clathrate is taken from Lectez et al. (2015).

From the examination of the condensation sequence presented in Fig. 4, we find that the hypothesis of O_2 agglomeration as pure crystalline ice is inconsistent with 67P/C-G’s current composition. The fact that Ar/CO and N_2/CO ratios are found to be significantly depleted by factors of ~ 90 and 10 in 67P/C-G’s coma, respectively, compared to the protosolar values (Rubin et al. 2015b; Balsiger et al. 2015; Mousis et al. 2016), implies that Ar and N_2 cannot form substantial amounts of pure crystalline ices at the formation location of the comet in the PSN (Mousis et al. 2016). Instead, it has been proposed that these volatiles were mostly trapped in CO-dominated clathrates (Mousis et al. 2016). Under these circumstances, because the equilibrium curve of O_2 ice is in the vicinity of those of Ar and N_2 ices, the incorporation of O_2 in this form would require the trapping of larger amounts of Ar and N_2 , incidentally leading to quasi protosolar Ar/CO and N_2/CO ratios. This does not agree with the depleted ratios observed in 67P/C-G.

6. CONCLUSIONS

In this study, we have investigated several scenarios that may explain the presence of molecular oxygen in the nucleus of 67P/C-G. Our results are the following:

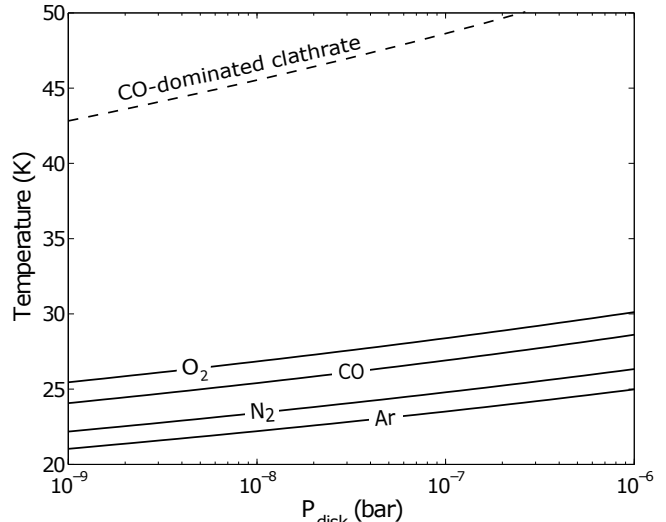


FIG. 4.— Solid lines: equilibrium curves of O_2 , CO, N_2 and Ar pure crystalline ices as a function of total disk pressure. Dashed line: equilibrium curve of the CO-dominated clathrate as a function of total disk pressure (see text).

- Even with a strong CRF enhancement due to the presence of a nearby supernova, we find that the radiolysis of icy grains is not fast enough in the PSN to create amounts of O_2 comparable with those observed in 67P/C-G. Instead, icy grains must be placed in low-density environments such as molecular clouds to allow radiolysis to work efficiently. The irradiation process also favors the stabilization of O_2 molecules in the icy matrix via the development of cavities and is compatible with both amorphous and crystalline ice structures.
- O_2 can be efficiently trapped in clathrates formed in the PSN. The O_2/CO ratio in the clathrate phase is up to ~ 2 times the O_2/CO ratio in the coexisting PSN gas phase.
- The incorporation of O_2 as pure crystalline ice is unlikely in 67P/C-G because the condensation of this species in the PSN would imply much larger abundances of Ar and N_2 than those observed in the coma.

Based on these results, and assuming that radiolysis has been the only mechanism for producing O_2 , we find that the formation of 67P/C-G is possible in a dense and early PSN in the framework of two extreme scenarios: (1) agglomeration from pristine amorphous icy grains/particles formed in the ISM and (2) agglomeration from multiple guest clathrates including O_2 that formed during the cooling of the disk subsequent to the vaporization of the amorphous icy grains entering the PSN. However, scenario 1 was found inconsistent with ROSINA pre-perihelion observations of volatile abundances in the coma. In contrast, Mousis et al. (2016) and Luspai-Kuti et al. (2016) have shown that scenario 2 could match these data if 67P/C-G agglomerated from a mixture of clathrates and crystalline ices that condensed in the PSN. Also, scenario 2 is compatible with a possible chemical production of O_2 in the PSN gas phase (Walsh et al.

2015). In this picture, whatever the considered source, i.e. radiolysis of ISM grains or/and PSN gas phase chemistry, O_2 is efficiently entrapped in clathrates prior to their agglomeration by 67P/C-G.

On the other hand, with the incorporation of O_2 in the cavities created by CRF in the icy matrix, scenario 1 naturally provides an explanation for the strong correlation found between the O_2 and H_2O production rates observed in 67P/C-G's coma (Bieler et al. 2015). If this scenario is correct, this would make implausible the accretion of 67P/C-G from clathrates and crystalline ices originating from the PSN. Meanwhile, a way to reconcile scenario 2 with the strong O_2 - H_2O correlation would be to assume that the icy grains initially formed as in scenario 1. These icy grains/particles would have then subsequently experienced an amorphous-to-crystalline phase transition in the 130–150 K temperature range when entering the disk (Kouchi et al. 1994; Maldoni et al. 2003; Ciesla 2014). In this alternative scenario, all volatiles initially adsorbed by ISM amorphous ice would be released in the PSN gas phase during phase transition. With the cooling of the disk, these volatiles would have been later trapped in the clathrates formed with the crystallized icy grains. The case of O_2 is unique because, due to its formation process, this molecule is inserted into the icy matrix. In spite of the phase transition, O_2 would remain stable within the icy matrix because the strength of the interaction between O_2 and the surround-

ing H_2O molecules is expected not to decrease (eventually increase) upon crystallization. In this scenario, CO, Ar, N_2 would be trapped in clathrates with O_2 remaining embedded in water, in a way consistent with the observed correlation.

To conclude, further post-perihelion ROSINA data, in particular the precise measurements of the relative abundances of the different volatiles as a function of geography and time, are needed to disentangle between the existing formation scenarios. It is also possible that only the in situ sampling of a nucleus by a future lander will provide a definitive answer to the question of the formation conditions of 67P/C-G and other Jupiter Family Comets in the PSN.

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